USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 385

EXTRACTABLE PETROLEUM HYDROCARBONS BY GC/FID

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1 PURPOSE AND APPLICABILITY

This procedure describes the determination of total petroleum hydrocarbons (TPH) as diesel range organics (DRO), assigned carbon rangeC_{10} - $C_{24,}$ and oil range organics (ORO), assigned carbon range C_{24} – $C_{40,}$ in extracts prepared from aqueous, solid and non-aqueous liquid samples. In instances where hydrocarbons in the sample more closely resemble other extractable petroleum hydrocarbon mixtures such as kerosene or hydraulic oil as determined by comparison to standards, a tentative hydrocarbon mixture identification is provided. This SOP is based on procedures contained in EPA SW-846 method 8015C, Revision 3, February 2007. Deviations from the reference method are described in Appendix A.

Water samples are prepared using EPA Region 9 Laboratory SOP 275 *Extraction of Water Samples by Continuous Liquid-Liquid Extraction*. Solid samples are prepared using EPA Region 9 Laboratory SOP 290 *Extraction of Soil Samples Using Pressurized Fluid Extraction.* Solid samples, including waste samples, may be prepared using EPA Region 9 Laboratory SOP 285 *Soxhlet Extraction of Solid Samples.* Waste samples and non-aqueous liquid samples may be prepared using EPA Region 9 Laboratory SOP 295 *Waste Dilution* if they are miscible with an appropriate solvent.

Modification of these procedures, such as quantitation based on hydrocarbon mixtures other than DRO and ORO or the use of silica gel cleanup to remove polar hydrocarbons must be arrange in advance through the Chemistry Technical Director.

Quantitation limits are provided in Appendix B by matrix and analyte.

2 METHOD SUMMARY

Sample extracts, which have been fortified with surrogate, are injected into a gas chromatograph (GC) with a flame ionization detector (FID). Sample components are separated in a fused-silica capillary GC column during temperature programming and detected by the FID.

Probable identification of fuels in samples is based on a comparison of the chromatographic pattern generated by analysis of the extract to the chromatographic pattern of known hydrocarbon fuel standards analyzed under the same conditions as the sample extract. The identification of specific fuel types may be complicated by substantial variation in fuel composition, and by environmental processes such as evaporation, biodegradation, or the presence of more than one fuel type. Data are qualified in a manner that reflects the qualitative uncertainty of the fuel identification.

The hydrocarbon concentration in the sample extract is determined by comparing the area sum response in the extract to the area sum response of hydrocarbon standards analyzed under the same conditions as the sample extract. The retention time range for the area response sum is determined from elution times of alkane hydrocarbons.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

DCM – Dichloromethane

MeOH - Methanol

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation must be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

4.1.1 Dichloromethane

Dichloromethane is a suspected carcinogen. Effects of overexposure: acute inhalation or ingestion causes mild central nervous system depression. The primary toxic effect is narcosis. Other toxic effects are pulmonary edema, encephalopathy, and hemolysis. Dichloromethane irritates the eyes, skin, and respiratory tract. No systemic effects have been reported in humans, although excessive concentrations have caused cancer and liver and kidney damage in animals. Emergency and first aid - Inhalation: immediately remove to fresh air. If not breathing, administer mouth-to-mouth rescue breathing. If there is no pulse, administer cardiopulmonary resuscitation (CPR). Contact physician immediately. Eye contact: flush with water continuously for 15 minutes. Get emergency medical assistance. Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothes and shoes. Get emergency medical assistance. Ingestion: call local poison

control center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

4.1.2 Acetone

Acetone liquid and vapors are highly flammable. Avoid heat, sparks, open flame, open containers, and poor ventilation. Effects of overexposure: Acetone is a mild eye and mucous membrane irritant, primary skin irritant, and central nervous system depressant. Acute exposure irritates the eyes and upper respiratory tract. Direct skin contact produces dermatitis, characterized by dryness and erythema through defatting of skin. High concentrations produce narcosis and hypoglycemia. Emergency first aid - Inhalation: immediately remove to fresh air. If not breathing, administer mouth-to-mouth rescue breathing. If there is no pulse, administer CPR. Contact physician immediately. Eye contact: flush with water continuously for 15 minutes. Get emergency medical assistance. Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothes and shoes. Wash clothing before re-use, and discard contaminated shoes. Get emergency medical assistance. Ingestion: call local poison control center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Flame ionization detectors use hydrogen gas as fuel. If hydrogen flow is on and no column is connected to the detector inlet fitting, hydrogen gas can flow into the oven and create an explosion hazard. Detector fittings must either be capped or have a column connected at all times.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure*. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or their designees.

This procedure produces the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
Sample Extracts	Hazardous Waste	See solvent, diesel fuel and motor oil MSDs

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Refer to EPA Region 9 Laboratory SOPs 275, 285, 290 or 295, as applicable (see Section 1).

5.2 Internal Chain-of-Custody

Sample extracts for GC analysis are received from the extraction laboratory personnel and custody transferred to the GC laboratory staff by signing the appropriate sections of the bench sheet.

The extracts are marked with the Region 9 Laboratory numbers and checked against the LIMS work order and chain-of-custody record to determine the client sample number, case number, and Sample Delivery Group (SDG) number.

5.3 Sample Extract Storage

Store sample extracts in the freezer in Room 406 maintained at $\leq$ -10 °C before and after analysis. Retain sample extracts under these conditions until the holding time has expired. Note that following analysis and reporting, the extracts must be stored an additional 60 days before segregating for disposal.

5.4 Extract Holding Time

Sample extracts must be analyzed within 40 days of extraction.

6 INTERFERENCES

6.1 Sample Matrix Interference

This method uses an FID – a relatively nonselective detector – so any combustible organic compounds present in the sample that are soluble in the extraction solvent may cause positive interferences. For example, polar hydrocarbons such as biogenic organics including lipids, plant oils, tannins, lignins, animal fats, proteins, humic acids, fatty acids, and resin acids may cause positive interference.

6.2 Extract contaminants

Chromatographic interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in chromatograms, or by carryover when low concentration extracts are analyzed after high concentration extracts. Specifically, phthalate esters are commonly used as plasticizers and are easily extracted from plastic materials. Avoid contacting samples, solvents, reagents, glassware, extracts, or other sample processing apparatus with plastic materials.

6.3 Carryover

Instrument contamination may occur when a sample extract containing low analyte concentrations is analyzed immediately after a sample extract containing relatively high analyte concentrations. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of an extract containing high analyte concentrations, a laboratory instrument blank should be analyzed to ensure that accurate values are obtained for the next sample.

Instrument contamination may occur when an extract containing oil range hydrocarbons, especially with carbon numbers exceeding C_{40}, is analyzed. After analysis of a sample extract containing oil range hydrocarbons, an instrument blank should be analyzed to ensure that accurate values are obtained for the next sample. The column may need to be heated to an elevated temperature, not exceeding the column limit, until the baseline returns to previous levels. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- Gas chromatograph with FID detector and splitless injection port (Agilent 6890, 7890, or equivalent).
- Fused silica capillary gas chromatography column – Any capillary column with a phase ratio (β) of about 265 that provides adequate resolution and capacity may be used. The column used for method validation was 15M x 0.32 mm x 0.1 µm Rtx-1.
- Data acquisition and processing system -- software to control the GC and acquire, store, and process gas chromatographic data. The software must be able to calculate calibration factors and the concentrations of analytes in sample extracts. Agilent Technologies EnviroQuant ChemStation software and data acquisition computers (or equivalent).

7.2 Reagents

All reagents must be entered into the LIMS.

- Acetone - capillary GC/GC-MS solvent grade.
  Caution: Acetone liquid and vapors are highly flammable. See Section 4.1.2 for precautions.

- Dichloromethane - recycled or capillary GC/GC-MS solvent grade.
  Caution: Dichloromethane is a suspected carcinogen. See Section 4.1.1 for precautions.

7.3 Standards

All standards must be entered into the LIMS.

7.3.1 Calibration Stock Standards:

The following standard composition and concentrations are recommended only; other mixtures and concentrations can be used as required by the project.

Description	Suggested Vendor and Catalog #	Compounds	Concentration
Diesel Fuel #2	Restek 31258	Diesel	50,000 µg/mL in DCM
Motor Oil	Restek 31464	Motor oil	50,000 µg/mL in DCM
Surrogate	INC Biomedical	N-Hexacosane ($n\text{-}C_{26}H_{54}$)	neat (1,000,000 µg/mL)
Second Source Diesel	Ultra Scientific RGO-616	Diesel Fuel	50,000 µg/mL in DCM
Second Source Oil	SPEX S-050W-20K	Motor oil, SAE50E	20,000 µg/mL in DCM
Florida TRPH n-alkane series	Restek 31266	C8-C40	500 µg/mL in hexane
Fuel Pattern Recognition	AccuStandard; FU-020D-40X	Hydraulic Fluid	20000 µg/mL in DCM
Fuel Pattern Recognition	AccuStandard HS-002S-40X	Mineral Spirits	20000 µg/mL in MeOH
Fuel Pattern Recognition	AccuStandard HS-003S-40X	Naphtha	20000 µg/mL in MeOH
Fuel Pattern Recognition	Restek 30205	Unleaded Gasoline	50000 µg/mL in MeOH
Fuel Pattern Recognition	Restek 31256	Kerosene Composite	50000 µg/mL in DCM
Fuel Pattern Recognition	AccuStandard FU-006-40X	Turbine (Jet) Fuel	20000 µg/mL in MeOH
Fuel Pattern Recognition	AccuStandard HS-004S-40X	Turpentine	20000 µg/mL in MeOH

Description	Suggested Vendor and Catalog #	Compounds	Concentration
Fuel Pattern Recognition	AccuStandard HS-001S-40X	Lacquer Thinner	20000 µg/mL in MeOH
Fuel Pattern Recognition	AccuStandard HS-005S-40X	Stoddard Solvent	20000 µg/mL in MeOH

Note: Check for project-specific quantitation requirements to determine if the instrument should be calibrated using an alternative mixture such as kerosene or a sample of the fuel or oil that is contaminating the site. The calibration standard should be selected prior to the start of the project in conjunction with the client.

7.3.2 Working Standards

- Surrogate Spiking Solution - Solution of n-hexacosane (n-$C_{26}H_{54}$) in dichloromethane:acetone 2:1 v/v at 2,500 µg/mL. Prepare from neat n-hexacosane by weighing 125 mg n-hexacosane into a 50 mL volumetric flask, dissolving it in 33 mL of dichloromethane (may require sonication or warming) and diluting to volume with acetone.

- Instrument Blank - Solution of n-hexacosane in dichloromethane at 50 µg/mL. Prepare from the surrogate spiking solution by diluting 1 mL to 50 mL in dichloromethane.

- TPH Matrix Spiking Solution - A solution of the fuel of interest at a concentration of 2,500 µg/mL in acetone. This solution is valid for six months from the date of preparation, or until ongoing QC indicates a problem exists, whichever is sooner.

- Calibration Verification Standard (CCV) - Equivalent to the mid-point initial calibration solution.

- Quantitation Limit Standard (QLS / CRL) - Equivalent to the lowest level calibration standard. The QLS is used to verify instrument response at the quantitation limit.

- Second Source Calibration Verification (SCV) – Approximately equivalent to the mid-point initial calibration solution but prepared from a source independent from the source of the calibration standards. The SCV is used to check the accuracy of the initial calibration solutions. See table above for suggested vendors for SCV standards.

7.3.3 Calibration Solutions

7.3.3.1 TPH solutions

The instructions provided below assume that the stock standards listed in section 7.3.1 are the source materials. If other stock standards are used, initial concentrations may vary – confirm dilution ratios prior to preparing the working standards.

Prepare TPH-DRO and TPH-ORO calibration solutions at five concentrations in dichloromethane from stock standard solutions. Recommended levels are shown in the tables below.

TPH-DRO Solution	Volume Used, µL	Final Volume, mL	Final Concentration, µg/mL
Stock Standard	10	10	50 (QLS)
Surrogate Spike	40	10	10
Stock Standard	30	10	150
Surrogate Spike	100	10	25
Stock Standard	100	10	500 (CCV)
Surrogate Spike	200	10	50
Stock Standard	250	10	1,250
Surrogate Spike	300	10	75
Stock Standard	800	10	4,000
Surrogate Spike	400	10	100

TPH-ORO Solution	Volume Used, µL	Final Volume, µL	Final Concentration, µg/mL
Stock Standard	40	10	200 (QLS)
Surrogate Spike	200	10	50
Stock Standard	80	10	400
Surrogate Spike	200	10	50
Stock Standard	200	10	1,000 (CCV)
Surrogate Spike	200	10	50
Stock Standard	800	10	4,000
Surrogate Spike	200	10	50
Stock Standard	2000	10	10,000
Surrogate Spike	200	10	50

7.3.3.2 Retention Time Standard (RT)

Prepare a standard containing the homologous n-alkane series covering the expected range at a concentration of 20 µg/mL. Prepare by diluting Florida TRPH standard in dichloromethane (e.g. dilute 40 µL of the 500 µg/mL stock to 1 mL).

7.3.3.3 Alternative Stock Standard Preparation

As an alternative to purchasing commercially available calibration solutions, standards may be prepared from neat fuels or oils as follows: Determine the density of the hydrocarbon fuel mixture by filling a tared 10 mL volumetric flask to volume with neat fuel at room temperature; record the weight in grams to the nearest 0.1 mg. Divide the net weight by 10 mL to obtain the density in g/mL. Use the experimentally determined density in the following calculations.

Prepare a 4,000 µg/mL (nominal) range standard by injecting 5 µL of neat standard per mL of dichloromethane. The actual concentration, in µg/mL, will be 5,000 times the density of the neat standard in g/mL. For example, injecting 250 µL of kerosene into about 49 mL of solvent in a 50 mL volumetric flask, then adding additional solvent to volume, would result in a 3,910 µg/mL standard assuming a density of 0.782 g/mL for kerosene.

If the neat standard, such as motor oil, is too viscous to measure with a microliter syringe, weigh out about 200 mg (0.2 g) using an analytical balance and dilute to 50 mL with dichloromethane.

Prepare the other calibration solutions by serially diluting the 4,000 µg/mL standard.

7.3.4 Storage of Standard Solutions

Store the unopened ampulated stock standard solutions at > 0°C to 6°C. Transfer opened stock standard solutions and all working standard solutions to glass bottles or vials with Teflon lined screw caps and store at ≤-10°C; protect all standards from light. Fresh standards should be prepared every six months, or sooner if comparison with check-standards indicates a problem. The standard solution must be checked frequently for stability. Replace all working standard solutions after six months or sooner if comparison with SCV indicates a problem.

CAUTION: Analysts must allow all standard solutions to equilibrate to room temperature before use. Hexacosane has poor solubility at low temperatures. Solutions containing hexacosane must be sonicated before use.

7.4 Supplies

- Volumetric flasks, type A, 100-mL, 50-mL, 25-mL, and 10-mL.
- Microliter syringes (10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1-mL).

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set up the instrument control parameters provided in Appendix D. Adjust as needed to meet method and SOP requirements. Instrument parameters must be the same between an initial calibration and all extracts quantitated using that calibration.

Prior to analyzing calibration or instrument QC make a LIMS sequence as required to obtain LIMS assigned IDs for the calibration and QC samples.

Ensure that all appropriate waste containers are properly connected and labeled.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

The initial calibration is a minimum 5-level external standard calibration using the mean CF for calculating analyte concentrations. See Section 9.2.1 of this SOP for required frequency.

Prepare calibration solutions according to Section 7.3.3.

Analyze each of the initial calibration standards and an instrument blank as described in Section 8.3. The following table shows an example initial calibration sequence:

Sequence	Sample Name
1	IB
2	RT
3	Level 1 DRO (QLS)
4	Level 2 DRO
5	Level 3 DRO (CCV)
6	Level 4 DRO
7	Level 5 DRO
8	Level 1 ORO (QLS)
9	Level 2 ORO
10	Level 3 ORO (CCV)
11	Level 4 ORO
12	Level 5 ORO
13	DRO SCV
14	ORO SCV
15-24	Fuel Pattern Recognition STDs (as needed)

Analyze each of the initial calibration standards and an instrument blank using the same instrument conditions to be used analyzing field sample extracts. Using the chromatography software and the following steps, calculate the average calibration factors and %RSD.

- Review the instrument blank to confirm that the analytical system is free of contamination.

- Review the RT standard to determine the elution time for C10, C24, and C40. Enter the carbon marker retention times into the method and obtain area sums for each fuel mixture in the designated time ranges using the following ranges: DRO:C_{10}– C_{24} and ORO:C_{24} – C_{40}

- Review the chromatograms and draw a manual baseline if the baseline drawn by the data system integrator does not accurately reflect the total area response, including the unresolved area that lies below the individual peaks, of the fuel. For DRO, draw a manual baseline beginning at the elution time of C10 to the elution time of C24. For ORO, draw a baseline beginning at the elution time of C24 and going to the elution time of C40. Manual integrations must conform to U.S. EPA Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures.* See Appendix E for example chromatograms.

- The data system calculates the calibration factor (CF) for the target fuel or n-alkane mixture from its area sum response and for the surrogate for all five calibration standards using Equation 1.

  Equation 1

  $$CF = (A_x)/ (C_x)$$

  Where
  Ax = Area of compound x
  Cx = Concentration of the standard injected (µg/mL)

- The data system calculates the average CF for all analytes.

- Using the above information, the data system calculates the percent relative standard deviation (%RSD) of the CF values for each compound using Equation 2.

Equation 2

$$\%RSD = (SD/ CF_{avg}) \times 100$$

Where SD is calculated as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - CF_{avg})^2}{n-1}}$$

Verify that the %RSD of both the target fuel(s) and surrogate are within QC limits immediately after the initial calibration is finished. See Appendix C for QC limits.

8.2.1.1 Retention Time Windows

Based on experience and historical data, the EPA Region 9 Laboratory uses a default retention time window of +/- 0.03 minutes for single component analytes. This approach is based on the insignificant retention time drift observed historically and the option listed in SW846 Method 8000C section 11.6 to select an alternative approach to the usual analysis of standards for the calculation of retention time windows.

To prevent false negatives, set the ChemStation window to ± 0.06 minutes so the software will identify peaks within the wider window and flag those which exceed the default retention time window with the "f" flag (the flag is added to peaks outside one half the ChemStation window) to prevent false negatives.

8.2.1.2 Second Source Calibration Verification (SCV)

Analyze a SCV standard immediately after each initial calibration. See Section 9.2.2 of this SOP for frequency and QC limits.

If the initial calibration, the SCV, and the IB meet all the criteria specified in Appendix C, the remainder of the analytical period may be used for the analysis of field and QC samples using the average CF from the initial calibration to quantitate the data.

8.2.2 Calibration Verification

Calibration verification is required at the beginning of each analytical period and at the end of the analytical period. The analytical period begins with the injection of the calibration verification standard and ends with the completion of

analysis of the last sample that can be injected within the period. Analysis of calibration verification standards after every ten samples is recommended to minimize the amount of re-runs necessary if a calibration verification should fail. The calibration verification standard is used to validate the initial calibration for the samples run during the associated period.

- Analyze an instrument blank and the calibration verification standard according to Section 8.3.

- Review the instrument blank to confirm that the analytical system is free of contamination.

- Calculate the calibration factor (CF) for the target fuel from its area sum response and for the surrogate compound using Equation 1.

- Calculate the percent difference (%D) between the calibration verification CF and the initial calibration average CF for the target fuel and the surrogate using Equation 3.

  Equation 3.

$$\%D = \frac{CF_c \times CF_{avg}}{CF_{avg}} \times 100$$

  Where:
  CF_c = calibration verification CF
  CF_{avg} = initial calibration average CF

The %D must be within QC limits. See Appendix C for QC criteria and section 9.2.3 for corrective action.

8.2.3 Quantitation Limit Standard

Analyze a standard of the fuel of interest at the concentration of the lowest initial calibration level according to Section 8.3 of this SOP and calculate the concentration of the target fuel.

Calculate the percent recovery for the target fuel using Equation 4.

Equation 4:

$$\%\ R = (\ Cd/Tv\ ) \times 100$$

Where:
%R = Percent Recovery
Cd = Concentration determined by analysis
Tv = True value of standard

See Section 9.2.4 for QLS requirements and Appendix C for QC limits.

8.3 Sample Analysis

8.3.1 Sample Extract Preparation

Sample extracts can be analyzed only after the initial calibration or calibration verification, QLS, MB, and IB meet all of the appropriate criteria specified in Appendix C.

Generate a LIMS sequence as required prior to analyzing QC or field sample extracts to obtain LIMS assigned IDs for the calibration and QC samples.

8.3.2 Analytical Sequence and Analysis

Set up a data acquisition sequence from the LIMS sequence using the GC control parameters used in the analysis of the initial calibration. The sample description shall include the laboratory sample ID. Additional header information should include the dilution factor, instrument ID, and the analyst's initials.

Include all QC sample extracts. It is highly recommended that the MB, BS, and MS/MSD extracts be analyzed as early as possible in the analysis of a batch.

The following table is an example field sample analysis sequence:

Sequence	Sample Name	Sequence	Sample Name
1	Priming	8	MB
2	IB	9	MS Sample
3	DRO CCV	10	MS
4	DRO QLS	11	MSD
5	ORO CCV	12-21	Field Samples
6	ORO QLS	22	DRO CCV
7	LCS	23	ORO CCV

8.3.3 Analyte Identification and Quantitation

After completion of analysis, review the chromatogram to identify the fuel in the sample. Compare the chromatographic pattern generated by analysis of the sample to the chromatographic pattern of fuels analyzed under the same conditions as the sample by visually comparing the printed chromatograms or by electronically overlaying the chromatograms, if needed.

Review the baseline drawn by the data system integrator to verify that it accurately reflects the area response of the fuel in the sample. If in the judgment of the analyst, it does not, then draw a manual baseline from the elution time of C10 to the elution time of C24. See Appendix E for examples. Document any manual integration following the procedure described in U.S. EPA Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures*.

Quantitate the chromatogram using the appropriate initial calibration mean CFs for the identified fuel. If applicable, indicate degree of similarity of sample chromatogram to the fuel to which it is being compared. Print out quantitation reports and chromatograms for each field and QC sample.

The fuel hydrocarbon mixtures, including diesel and oil, contain large numbers of chemical components which overlap. Use the following tables to report the diesel and oil ranges:

<table>
<tr><td>Report</td><td colspan="4">Chromatogram indicates the presence of:</td></tr>
<tr><td></td><td>Diesel Fuel Only</td><td>Motor Oil Only</td><td>Both Diesel Fuel and Motor Oil</td><td>Other hydrocarbon mixtures</td></tr>
<tr><td>DRO: C_{10}-C_{24}</td><td>Quantitate against the TPH-diesel range standard and report. Apply the appropriate LIMS flag to describe the fuel or product type (examples below).</td><td>Quantitate the overlap area against the TPH-diesel range standard and report the value as “non-detect” U at that concentration (i.e. raise the sample QL).</td><td rowspan="2">Draw both integrations to the respective alkane markers and report both fuels
Apply the appropriate LIMS flags for each to describe the fuel or product types (examples below).</td><td>Quantitate, the area in the DRO range.
Apply the appropriate LIMS flag to describe the fuel or product type (examples below).</td></tr>
<tr><td>ORO: C_{24}-C_{40}</td><td>Quantitate the overlap area against the oil range standard and report the value as “non-detect” U at that concentration (i.e. raise the sample QL).</td><td>Quantitate against the oil range standard and report.
Apply the appropriate LIMS flag to describe the fuel or product type (examples below).</td><td>Quantitate, area in the ORO range.
Apply the appropriate LIMS flag to describe the fuel or product type (examples below).</td></tr>
</table>

LIMS Qualifier Flags

LIMS Flag	Description
F0	[CUSTOM]
F2	Fuel Type: Gasoline
F3	Fuel Type: Kerosene or Jet Fuel
F4	Fuel Type: Diesel
F5	Product Type: Motor Oil
F6	Product Type: Hydraulic Fluid
F7	Product Type: Lacquer Thinner
F8	Product Type: Mineral Spirits
F9	Product Type: Naphtha
F10	Product Type: Stoddard Solvent
F11	Product Type: Turpentine
F12	Single component, unidentified
F13	Fuel or Product Type: mixed or unknown

All detected results should be flagged in LIMS using the above designations to characterize the product or fuel type. If a mixture is present, multiple flags may be appropriate (diesel and motor oil, kerosene and hydraulic fluid). Use the F0 flag to briefly narrate further information when it is available (e.g. Single component, tetrachloroethene identified by GCMS).

In the event that the client provides a fuel/product for calibration, the Technical Director will enter a project specific LIMS analysis. Use the F0 flag to indicate if the reported concentration resembles the standard used for calibration. If the sample contains a known product or fuel, use the appropriate flag, but quantitated against the client standard unless otherwise instructed. Describe the standard and calibration procedure in the work order memo field.

- Water calculations

  Calculate results for target analytes using Equation 5:

  Equation 5:

$$\text{Conc. ug / L} = \frac{A_x \times V_t \times DF}{CF \times V_o}$$

  Where:

  A_x = area sum response of the sample
  DF = dilution factor
  CF = mean calibration factor from the initial calibration
  V_o = volume of water extracted in Liters
  V_t = volume of concentrated extract in mL

- Soil calculations

  Calculate results for target analytes using Equation 6:

  Equation 6:

$$\text{Conc. mg/kg (dry weight basis)} = \frac{A_x \times V_t \times DF}{CF \times W \times D}$$

  Where:

A_x	= area sum response of the sample
D	= dry weight factor (Percent solids/100)
W	= weight of sample in grams
CF	= mean calibration factor from the initial calibration
V_t	= volume of concentrated extract in mL
DF	= dilution factor

  Yields concentration units of µg/g = mg/kg

- Check surrogate recovery for each sample with criteria in Appendix C.

- Dilute and inject a new aliquot of the extract if the on-column concentration of the fuel of interest in any sample exceeds the initial calibration range. Use the following criteria in performing dilutions:

  1. Use the results of the original analysis to determine the approximate dilution factor required to get the fuel of interest within the initial calibration range.
  2. Do not dilute MS/MSD samples to get either the spiked or non- spiked target compounds within the initial calibration range. If the sample from which the spike aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis, and note the problem in the work order memo field.
  3. In the case of extremely contaminated samples several dilutions may be required.
  4. Demonstrate that there is no carryover to subsequent analyses after a sample is analyzed that contains compounds at a level exceeding the initial calibration range of the system. This can be done by analyzing an instrument blank.
     Review the results for the sample analyzed immediately after a contaminated sample for all compounds that were in the contaminated sample that exceeded the limits above. The sample should not contain

a concentration above the QL for the target compound that exceeded the limits in the contaminated sample.

5. The most common cause of carryover is due to hydrocarbons in the oil/asphalt range. Cleaning the injection port and baking out the column may be required.

8.3.4 Data and QC Review

Review results of instrument QC (CV, QLS) immediately after their analysis to verify that the results are within QC limits. If the instrument QC results are not within QC limits, stop the sequence and take corrective action before resuming the sequence. See Section 9.2; see Appendix C for QC limits.

Review results of batch QC (MB, BS, MS/MSD). See Section 9.3; see Appendix C for QC limits.

Review results of sample QC (surrogate recovery). See Section 9.4; see Appendix C for QC limits.

8.3.5 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS.

LIMS will report all results to two significant figures and detected results to one-half the QL. LIMS flags values between one-half the QL and the QL as estimated (J); the analyst must manual add a "C1" flag to these results.

8.3.6 Instrument Maintenance

The following are suggested remedial actions that may improve method performance; re-calibration may be necessary after most of these actions:

- Check and adjust GC operating conditions and temperature programming parameters.
- Clean or replace the splitless injector liner with a new, silanized liner.
- Cut off a short portion of the GC column from the end near the injector, or replace the column. Cutting off a portion of the column will somewhat shorten the analyte retention times.
- Prepare fresh calibration solutions and repeat the initial calibration.
- Replace any components in the GC that permit analytes to come in contact with hot metal surfaces.

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook. Preventative maintenance procedures are listed in Appendix F.

The following sections describe possible causes and corrective actions for common problems. Refer to Appendix F for routine preventative maintenance procedures and schedule.

Symptom

- Carryover
  Possible causes: Analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.
  Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.
  Possible cause: column flow rate problem.
  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Loss of resolution.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: Check for leaks, replace septum, replace the liner, replace inlet seal, clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory

solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of the QC Criteria is provided in Appendix C.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in U.S. EPA Region 9 Laboratory SOP 880. *Demonstration of Capability*

9.2 Instrument QC

9.2.1 Initial Calibration

Demonstration and documentation of an acceptable initial calibration are required before any samples are analyzed. The calibration is an external standard calibration method.

The GC system must be calibrated whenever corrective action changes instrument response (e.g., detector gas adjustment, column replacement, etc.) is performed or if the calibration verification criteria cannot be met.

- Review the alkane standard to confirm that the correct elution times for C10, C24, and C40 are entered into the method to obtain area sums for each fuel mixture in the designated time ranges.

- Verify that the %RSD of the target fuel(s) and surrogate are within QC limits. See Appendix C for QC limits.

- If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the failed one in the ICAL. If more than one standard fails, corrective action is required.

9.2.2 SCV Analysis

An SCV sample is analyzed immediately after each initial calibration. See Appendix C for QC limits. If the SCV sample fails it may be repeated once. If the second SCV fails, the cause for failure must be determined and corrected before analysis of samples can proceed.

Note: Fuel standards from different sources may contain different compound mixes and therefore may not be reliable for verifying calibration standards. Seek technical guidance from the group leader should the SCV fail repeatedly.

9.2.3 Calibration Verification

See Appendix C for QC for frequency and %D requirements. The %D must be within QC limits. If an analyte fails this criterion a second calibration verification may be analyzed. Repeated failure requires that corrective action be taken to restore the system before any additional samples are analyzed. All affected samples must be re-analyzed.

If significant repairs to the system are required then a new initial calibration must be performed. The analyst should observe trends in the data such as declining response, erratic response, etc., which may signal the need for instrument maintenance.

Reported sample analyses must be bracketed by the analyses of calibration verification standards that meet QC limits.

9.2.4 Quantitation Limit Standard (QLS)

See Appendix C for QC for frequency and %R requirements. The %R must be within QC limits. If an analyte fails this criterion a second QLS may be analyzed. Repeated failure requires that corrective action be taken to restore the system before any additional samples are analyzed. All affected samples must be re-analyzed.

9.2.5 Instrument Blank (IB)

Analyze an instrument blank at the beginning of each analytical sequence, or after any high level sample. The instrument blank chromatogram and quantitation report must be checked to insure it is within QC limits in Appendix C. It is also important to monitor the chromatographic baseline to insure there are no humps or disruptions which could be integrated as peak area when sample constituents elute on top of them. Surrogate recovery is not evaluated for IB samples. If the instrument blank meets these requirements sample analysis may proceed.

9.3 Batch QC

Equations for calculating percent recovery (%R) and relative percent difference (RPD) are found in section 27.2.2 of the LQAP.

9.3.1 Method Blank

- A method blank (MB) is extracted and analyzed with each extraction batch to demonstrate that the entire analytical system - from extraction through GC analysis - is free of contamination.

- Analyze the MB according to Section 8.

- Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- Corrective action - If the MB is not acceptable, the source of the contamination must be found and eliminated and the problem documented before analysis can proceed. If re-analysis does not solve the problem, the batch may have to be re-extracted. Corrective action is decided by the EPA Chemistry Technical Director on a case by case basis.

- If the surrogate recovery does not meet acceptance criteria, re-analyze the extract. If the surrogate recovery fails high and the analytes in the blank are $\leq$ ½ the QL, report and narrate. If the surrogate fails low, all samples in the batch that are not ND may have to be re-extracted. Corrective action is decided by the EPA Chemistry Technical Director on a case by case basis.

9.3.2 Laboratory Control Sample

- Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. A LCS is extracted and analyzed once per extraction batch. The LCS is a MB spiked with laboratory fortified matrix solution.

- Analyze a LCS containing the target fuel according to Section 8 of this SOP.

- Calculate the percent recovery (%R) and compare to the QC limits in Appendix C. If acceptable accuracy cannot be achieved, the problem must be located and corrected prior to reporting any sample data and before additional samples are analyzed.

9.3.3 Matrix Spike/Matrix Spike Duplicate

- Laboratory fortified matrix (MS) and duplicate (MSD) samples are extracted and analyzed for the same matrix in an SDG. Additionally, all client-specified matrix QC samples must be prepared and analyzed. If there are no client-specified matrix QC samples, the extraction analyst will choose one representative sample for QC analysis. The extraction analyst shall not designate any obvious field blanks as the QC sample.

- If there is insufficient volume of sample to perform a matrix QC, it must be documented in the LIMS work order memo field and work order case narrative of the final report to notify clients.

- Analyze the MS/MSD extracts according to Section 8 of this SOP as soon as possible following the analysis of the sample designated as the laboratory fortified matrix sample.

- Calculate the percent recovery (%R) and relative percent differences (RPD) in the MS and MSD. See Appendix C for QC limits.

  The MS/MSD recovery limits are advisory only. If the limits are not met, no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 20% of expected values.

- The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX+ = PASS ! = FAIL								
CASE	1	2	3	4	5	6	7	8
BS - %R	+	+	+	+	!	!	!	!
MS/MSD -%R	+	!	+	!	+	!	+	!
MS/MSD - RPD	+	+	!	!	+	+	!	!

Case 1: Extraction batch acceptable.

Case 2: Extraction batch acceptable; matrix effect confirmed.

Cases 3 & 4: Extraction batch is unsatisfactory. Investigate MS/MSD problem and document findings in work order memo field.

Case 5: Extraction batch rejected. Batch may have to be re-extracted unless LCS problem is determined and documented.

Cases 6, 7 & 8: Extraction batch rejected. Re-extract batch.

9.4 Sample QC

9.4.1 Surrogate Recovery

- Calculate the surrogate recovery in all field and QC samples immediately after analysis using the following formula:

Equation 7:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

- The surrogate recovery must be within QC limits. See Appendix C for QC limits.

- Take the following steps if surrogate recovery is not within the limits:

  1. Ensure that there are no calculation errors, and check the system performance.
  2. Re-analyze the extract if a system performance problem or calculation error is not evident. The extract may be diluted for re-analysis if examination of the chromatogram so indicates.
  3. If re-analysis of the extract does not solve the problem, the sample may have to be re-extracted. Corrective action is decided by the EPA Chemistry Technical Director on a case by case basis.

- Do not re-extract undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the run log.

- Do not re-analyze the MS or MSD samples, even if surrogate recoveries are outside the limits.

- If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis. The similarity in surrogate recoveries in the sample and spike analyses must be discussed in the work order memo field.

- If the surrogate recoveries of the re-analysis of the extract are within limits, then:

  1. If the re-analysis was undiluted, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. The LIMS distinguishes between the analysis and re-

analysis by adding an "RE" suffix to the client sample ID on the re-analysis. The problem must be documented in the work order memo field.

2. If the re-analysis was diluted, the problem was a matrix effect. Report the results from the re-analysis and submit the data from both analyses and discuss the result in the work order memo field. The problem must be documented in the work order memo field.
3. If the surrogate recoveries of the re-extraction are within limits, then the problem was within the laboratory's control. Report the results from the re-extraction. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the client sample ID in the re-analysis. The problem must be documented in the work order memo field.

- If the re-extraction does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the client sample ID in the re-analysis. The problem must be documented in the work order memo field.

9.5 Method Performance

The following table summarizes method performance by matrix for the period 11/13/12 to 11/13/13.

Method Performance

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2σ)
Diesel	Water	LCS	35	84.1	67.5 – 101
Diesel	Solid	LCS	42	86	67.7 - 104

The primary sources of analytical error are:

- Poor extraction efficiency due to specific analyte characteristics or other problems.
- Standard degradation
- Chromatographic separation and peak integration.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QL, MS/MSD, and LCS) are recorded in the LIMS. A

copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

Document the analytical sequence in the LIMS.

Record the instrument ID and the LIMS calibration ID for each sequence. Record the Laboratory number, analysis, position, and LIMS standard ID, as applicable for each field and QC sample in the Element analysis sequence.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records. EPA Region 9 Laboratory SOP 845 *Analytical Data Review* provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control. Document all preventive or routine maintenance performed, as well as repairs or corrective or remedial actions in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Distribution and Acknowledgement

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Lab QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained in the LotusNotes database in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix G.

11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on LotusNotes or the local area network (G:\USER\SHARE\QA PROGRAM\LAB SOPS PDF) for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

Agilent Technologies 6890 Gas Chromatograph Users Manual

Agilent Technologies 7890 Gas Chromatograph Users Manual

Agilent Technologies EnviroQuant ChemStation User's Guide

U.S. Environmental Protection Agency, *Method 8000C, Determinative Chromatographic Separations, Revision 3, March, 2003.*

U.S. Environmental Protection Agency, *Method 8015C, Nonhalogenated Organics Using GC/FID, Revision 3, Feb. 2007.*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. In the SOP, the retention time range for Diesel Range Organics is C_{10} to C_{24} based on the analysis of an n-alkanes standard, not the retention time of C_{10} to C_{28} alkanes specified in the reference method. In addition, the SOP extends the chromatographic range of the method to include Oil Range Organics C_{24} to C_{40}.

2. The CF is area/concentration unit (µg/mL) not area/mass (ng) as in the reference method. The formulas for determining sample analyte concentrations have been modified to reflect this change.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

Hydrocarbon Fuel	On column, µg/mL	Solid, mg/kg (30g sample)	Water, µg/L (1 L sample)
TPH – Diesel Range Organics	50	5	150
TPH – Oil Range Organics	200	20	600

APPENDIX C.
CONTROL MEASURES AND CRITERIA

QC Measure		Criteria	Frequency
ICAL RSD		≤ 20%	After failure of CCV, with each ICAL
CCV %D		≤ 20%	Opening and closing per 12 hour sequence
SCV %D		≤ 30%	With each ICAL
LCS[1] %R	Water Solid	59 – 109% 59 – 113%	1/extraction batch or 20 samples
MB		<½ QL	1/extraction batch or 20 samples
QLS %R		60-140%	Beginning of sequence and every 40 samples
MS and MSD[1], %R	Water Solid	50 – 126% 21 – 112%	1/SDG or 20 samples[2]
MS/MSD[1], RPD	Water Solid	≤ 37% ≤ 50%	1/SDG or 20 samples[2]
Sample Retention Time Drift		±0.03 minutes	Method setup
IB		<½ QL	As necessary
Surrogate %R	Water Solid	47- 130% 20 - 111%	With each sample

[1] Spiked with diesel.
[2] Whichever is more frequent

Note: limits are based on data from November 13, 2012 to November 13 2013.

APPENDIX D.
RECOMMENDED INSTRUMENT CONTROL PARAMETERS

AG6890-4 GC METHOD

OVEN
Initial temp: 50 'C (On) Maximum temp: 350 'C
Initial time: 2.00 min Equilibration time: 0.50 min
Ramps:

#	Rate	Final temp	Final time
1	25.00	330	10.00
2	0.0(Off)		

Post temp: 0 'C
Post time: 0.00 min
Run time: 23.20 min

FRONT INLET (SPLIT/SPLITLESS)
Mode: Pulsed Splitless
Initial temp: 320 'C (On)
Pressure: 5.33 psi (On)
Pulse pressure: 10.0 psi
Pulse time: 0.40 min
Purge flow: 40.0 mL/min
Purge time: 0.30 min
Total flow: 44.9 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 2.00 min
Gas type: Helium

BACK INLET (SPLIT/SPLITLESS)
Mode: Pulsed Splitless
Initial temp: 320 'C (On)
Pressure: 2.33 psi (On)
Pulse pressure: 10.0 psi
Pulse time: 0.40 min
Purge flow: 48.2 mL/min
Purge time: 0.30 min
Total flow: 52.2 mL/min
Gas saver: Off
Gas type: Helium

COLUMN 1
Capillary Column
Model Number: Restek RTX-1
15M x 0.32mm x 0.1um df
Max temperature: 350 'C
Nominal length: 15.0 m
Nominal diameter: 320.00 um
Nominal film thickness: 0.10 um
Mode: constant flow
Initial flow: 2.0 mL/min
Nominal init pressure: 5.33 psi
Average velocity: 38 cm/sec
Inlet: Front Inlet
Outlet: Front Detector
Outlet pressure: ambient

COLUMN 2
Capillary Column
Model Number: Restek RTX-1
Max temperature: 350 'C
Nominal length: 15.0 m
Nominal diameter: 320.00 um
Nominal film thickness: 10.00 um
Mode: ramped pressure
Initial pressure: 2.33 psi
Initial time: 0.00 min

#	Rate	Final pres	Final time
1	0.0(Off)		

Post pressure: 0.00 psi
Nominal initial flow: 0.6 mL/min
Average velocity: 15 cm/sec
Inlet: Back Inlet
Outlet: Back Detector
Outlet pressure: ambient

FRONT DETECTOR (FID)
Temperature: 350 'C (On)
Hydrogen flow: 40.0 mL/min (On)
Air flow: 440.0 mL/min (On)
Mode: Constant makeup flow
Makeup flow: 49.0 mL/min (On)
Makeup Gas Type: Nitrogen
Flame: On
Electrometer: On
Lit offset: 2.0

BACK DETECTOR (FID)
Temperature: 350 'C (On)
Hydrogen flow: 40.0 mL/min (On)
Air flow: 440.0 mL/min (On)
Mode: Constant makeup flow
Makeup flow: 49.0 mL/min (On)
Makeup Gas Type: Nitrogen
Flame: On
Electrometer: On
Lit offset: 2.0

SIGNAL 1
Data rate: 10 Hz
Type: front detector
Save Data: On
Start Save Time: 1.30 min
Stop Save Time: 20.00 min
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 10 Hz
Type: back detector
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
Derive from front detector

COLUMN COMP 2
Derive from back detector

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint

7673 Injector

Front Injector:
Sample Washes 2
Sample Pumps 3
Injection Volume 2.0 microliters
Syringe Size 10.0 microliters
PostInj Solvent A Washes 3
PostInj Solvent B Washes 3
Viscosity Delay 0 seconds
Plunger Speed Fast
PreInjection Dwell 0.00 minutes
PostInjection Dwell 0.00 minutes

Back Injector:
No parameters specified

Column 1 Inventory Number : RTX-1 15M
Column 2 Inventory Number : RTX-1B

AG7890-2 METHOD

C:\MSDCHEM\1\2012\METHOD\012712DROA.M
Fri Dec 28 14:14:51 2012

Control Information
Sample Inlet : GC
Injection Source : Manual

Oven
Equilibration Time 0.5 min
Max Temperature 330 degrees C
Slow Fan Disabled
Oven Program On
50 °C for 2 min
then 95 °C/min to 115 °C for 0 min
then 65 °C/min to 175 °C for 0 min
then 45 °C/min to 330 °C for 6 min
Run Time 13.052 min

Front Injector
Syringe Size 10 µL
Injection Volume 2 µL
Solvent A Washes (PreInj) 3
Solvent A Washes (PostInj) 3
Solvent A Volume 8 µL
Solvent B Washes (PreInj) 3
Solvent B Washes (PostInj) 3
Solvent B Volume 8 µL
Sample Washes 2
Sample Wash Volume 8 µL
Sample Pumps 3
Dwell Time (PreInj) 0 min
Dwell Time (PostInj) 0 min
Solvent Wash Draw Speed 300 µL/min
Solvent Wash Dispense Speed 6000 µL/min
Sample Wash Draw Speed 300 µL/min
Sample Wash Dispense Speed 6000 µL/min
Injection Dispense Speed 6000 µL/min
Viscosity Delay 0 sec
Sample Depth Disabled
Injection Type Standard

L1 Airgap	0.2 µL

Back Injector

Syringe Size	10 µL
Injection Volume	1 µL
Solvent A Washes (PreInj)	3
Solvent A Washes (PostInj)	3
Solvent A Volume	8 µL
Solvent B Washes (PreInj)	3
Solvent B Washes (PostInj)	3
Solvent B Volume	8 µL
Sample Washes	0
Sample Wash Volume	8 µL
Sample Pumps	3
Dwell Time (PreInj)	0 min
Dwell Time (PostInj)	0 min
Solvent Wash Draw Speed	300 µL/min
Solvent Wash Dispense Speed	6000 µL/min
Sample Wash Draw Speed	300 µL/min
Sample Wash Dispense Speed	6000 µL/min
Injection Dispense Speed	6000 µL/min
Viscosity Delay	0 sec
Sample Depth	Disabled
Injection Type	Standard
L1 Airgap	0.2 µL

Sample Overlap
Sample overlap is not enabled

Front SS Inlet He

Mode	Pulsed Splitless
Heater	On 320 °C
Pressure	On 5.3292 psi
Total Flow	On 45 mL/min
Septum Purge Flow	On 3 mL/min
Gas Saver	On 20 mL/min After 1.5 min
Injection Pulse Pressure	10 psi Until 0.4 min
Purge Flow to Split Vent	40 mL/min at 0.3 min

Back SS Inlet He

Mode	Pulsed Splitless
Heater	On 320 °C
Pressure	On 5.339 psi
Total Flow	On 45.004 mL/min
Septum Purge Flow	On 3 mL/min
Gas Saver	On 20 mL/min After 1.5 min
Injection Pulse Pressure	10 psi Until 0.4 min
Purge Flow to Split Vent	40 mL/min at 0.03 min

Column #1
Restek 10106: 1730.60105
Rtx-1
330 °C: 15 m x 320 µm x 0.1 µm
In: Front SS Inlet He
Out: Front Detector FID

(Initial)	50 °C
Pressure	5.3292 psi
Flow	2 mL/min
Average Velocity	37.778 cm/sec
Holdup Time	0.66176 min
Flow Program	Off
2 mL/min for 0 min	
Run Time	13.052 min

Column #2
Restek 10106: 1730.60105
Rtx-1
330 °C: 15 m x 320 µm x 0.1 µm
In: Back SS Inlet He
Out: Back Detector FID

(Initial)	50 °C
Pressure	5.339 psi
Flow	2.0043 mL/min
Average Velocity	37.847 cm/sec
Holdup Time	0.66056 min
Flow Program	Off
2.0043 mL/min for 0 min	
Run Time	13.052 min

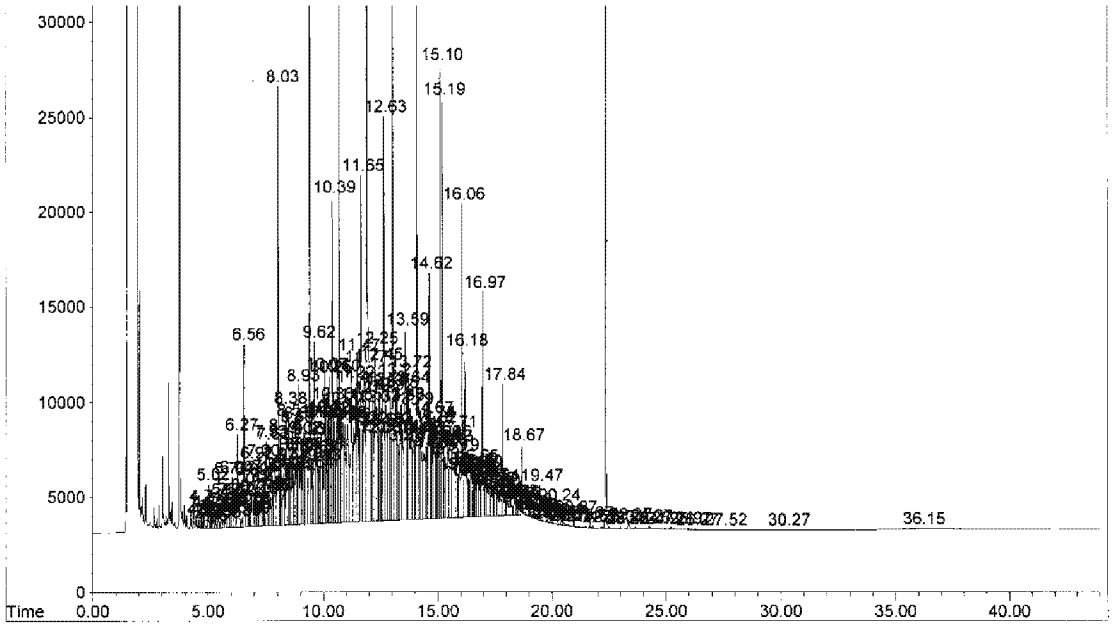
Front Detector FID	
Heater	On 350 °C
H2 Flow	On 40 mL/min
Air Flow	On 440 mL/min
Makeup Flow	On 47.8 mL/min
Const Col + Makeup	On 49.8 mL/min
Flame	On
Electrometer	On

Back Detector FID	
Heater	Off
H2 Flow	Off
Air Flow	Off
Makeup Flow	Off

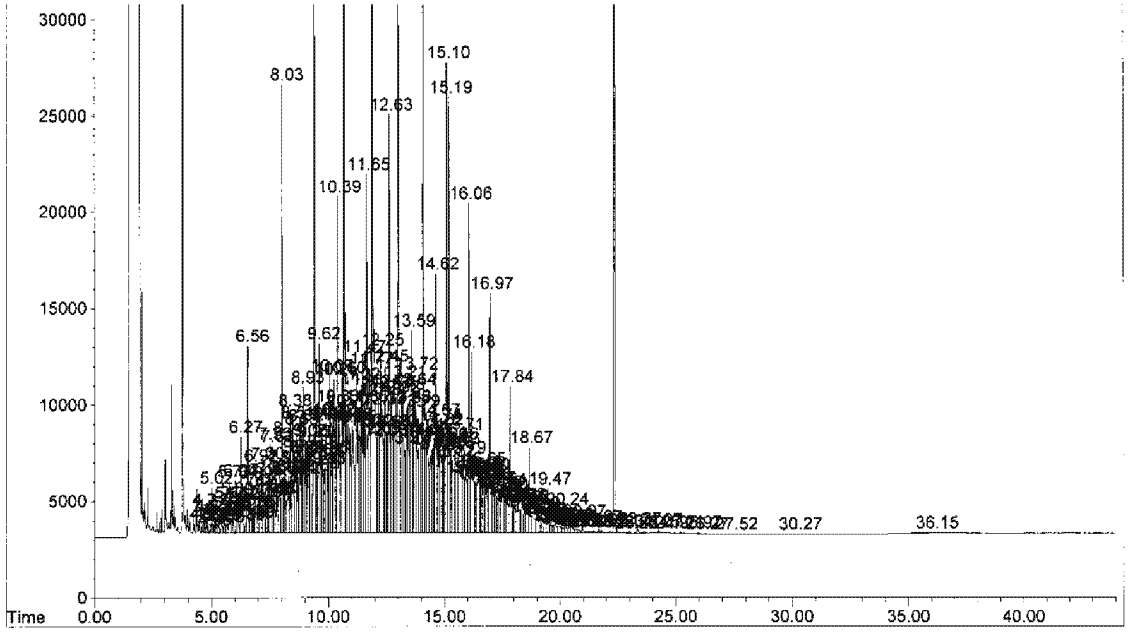
Const Col + Makeup Off
Flame Off
Electrometer On

Signals
Signal #1: Front Signal Save On
10 Hz
Signal #2: Back Signal Save Off
50 Hz
Signal #3: Test Plot Save Off
50 Hz
Signal #4: Test Plot Save Off
50 Hz

APPENDIX E.
INTEGRATION EXAMPLES



INCORRECT BASELINE INTEGRATION



CORRECT BASELINE INTEGRATION

APPENDIX F.
PREVENTIVE MAINTENANCE REQUIREMENTS

Item	Frequency	Actions/Comments
Split vent trap	As Needed	Replace.
Flowmeter calibration	2 years	Manual flowmeters only.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	With each ICAL	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Replace with liner or with signs of wear.
Inlet septum	Daily (when analyzing samples)	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	As Needed	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	As Needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Solvent rinse	As needed	When chromatography degradation is due to column contamination. Only for bonded and cross-linked phases.
Replacement	As needed	When trimming and/or solvent rinsing no longer return chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.
FID Jets & Collector	As needed	Clean when deposits are present. Replace when they become scratched, bent, or damaged, or when having difficulty lighting FID or keeping flame lit.
Purge/Sample Lines	As needed	Bake out and purge. Clean with organic free water if necessary.
Trap	As needed	Replace when loss of performance.

APPENDIX G.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 385
Revision: 5, Effective: 3/21/14

EXTRACTABLE PETROLEUM HYDROCARBONS BY GC/FID

Revision	Effective Date	Description
4	08/15/10	1. Changed reference method to EPA 8015C. 2. Revised quantitation and reporting procedures.
5	3/21/2014	1. Update historical control limits and method performance. 2. Include new instrumentation. 3. Updated reporting limit for water for consistency with QLS and solids. 4. Revise to current SOP 850 and laboratory practices and completed general edits throughout.